JOURNAL OF Materials CHEMISTRY

Dispersion of nano-sized gold particles into polymers: dependence on terminal groups of polymers and morphology of vapor-deposited gold

Shigehito Deki,*[a] Koichi Sayo,[a] Toshiyuki Fujita,[a] Atsushi Yamada[a] and Shigehiko Hayashi[b]

[a]*Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1–1, Rokkodai-cho, Nada-ku, Kobe 657–8501, Japan. E-mail: deki@kobe-u.ac.jp*
[b]*Mitsuboshi Belting Ltd., 4–1-21, Hamazoe-dori, Nagata-ku, Kobe 653–0024, Japan*

Received 4th January 1999, Accepted 5th February 1999

Dispersion of nano-sized gold particles into polymers was investigated from the viewpoint of terminal groups and molecular motion of the matrix polymers, and from morphology of vapor-deposited gold. NH_2-terminated poly(ethylene oxide) (PEO-NH_2) and poly(ethylene glycol) (PEG) were used as the matrix polymers. When gold with a thickness of 20 nm was vapor-deposited onto a melt of PEO-NH_2 at 60 °C, nano-sized gold particles were smoothly dispersed into the melt. On the other hand, gold vapor-deposited on a melt of PEG formed only conglomerates. When gold with a thickness of 3 nm was vapor-deposited onto PEO-NH_2 and PEG films kept at 20 °C, it formed particulate films. The gold particles formed were not dispersed into the polymer films by heat-treatment below the melting point of the polymer. However, when the polymer films were melted by heat-treatment at 50 °C, the gold particles were dispersed only into PEO-NH_2. When gold with a thickness of 20 nm was vapor-deposited on the polymer films, it formed conglomerates, therefore the dispersion of gold particles into both polymers was not observed even upon heat-treatment at 50 °C. Measurements of spin–spin relaxation time by solid-state ^{1}H NMR indicated that the molecular motion of PEO-NH_2 was restricted below the melting point. Therefore, the dispersion of the nano-sized particles occurred only above the melting point of PEO-NH_2.

Introduction

As the interest in the physical properties of nano-sized metal particles increases,[1–3] various kinds of preparation methods for nano-sized metal particles have been developed in vacuum or in solutions.[4] Vapor deposition is a very useful method for obtaining nano-sized metal particles on solid substrates, but the availability of the nano-sized particles thus formed is restricted and mass production of mono-dispersed particles is difficult. Chemical reactions in solutions are also popular for producing nano-sized metal particles stabilized by surfactants, but the concentration of nano-sized metal particles thus obtained is low.

Polymers are useful materials for the protection of nano-sized particles against agglomeration and precipitation.[5] Many studies on polymer-protected metal particles have been carried out,[6–9] and a variety of approaches have been reported.[10–12] In most cases, metal precursors were used as the sources of the metals, but they require moderate reaction conditions and long reaction times to obtain small particle sizes, a narrow size distribution, and well-separated particles.

We have studied the formation of nano-sized metal particles in a polymer matrix,[13,14] and recently, we found a novel dispersion phenomenon of nano-sized particles into a melt of poly(ethylene oxide) having NH_2 terminal groups. The phenomenon provides an excellent one-step preparation method of a solid composite in which nano-sized metal particles are dispersed separately from each other. The composite is water-soluble and it is possible to produce a colloidal solution. The nano-sized gold particles are stable for more than a year in the composite and the colloidal solution. In addition, the solid composite is recovered from the colloidal solution. In this paper, we investigate the dispersion of nano-sized gold particles into polymers from the viewpoint of terminal substituents and molecular motion of polymers, and from the morphology of vapor-deposited gold.

Experimental

Poly(ethylene oxide) having NH_2 terminal groups (PEO-NH_2, Scientific Polymer Products) and poly(ethylene glycol) (PEG, Wako Pure Chemical Industries) were used as matrix polymers. The average molecular weight of both polymers was *ca.* 2000. They were white waxy solids and melted at 48–50 °C. The content of NH_2 groups in PEO-NH_2 was 0.08 Mequiv. g^{-1}.

Thin matrix films of PEO-NH_2 and PEG were formed by casting a 40 wt% acetone solution of each polymer on glass substrates. The thickness of the films was *ca.* 15 μm. Gold (Tanaka Kikinzoku, 99.99%) was vapor-deposited from an alumina-coated tungsten basket onto the thin films of PEO-NH_2 and PEG in an ULVAC EBH-6 evaporator under a vacuum of *ca.* 6.7×10^{-3} Pa. The temperature of the substrates was kept at 0, 20, or 60 °C during the vapor-deposition. At the substrate temperature of 60 °C, the polymers melted, but the possibility of sublimation of the polymers was negligible because the vacuum pressure did not change during the vapor-deposition. The samples were taken out from the evaporator after the substrates returned to room temperature in a vacuum. The deposition rate of gold was *ca.* 6 nm min^{-1} and was monitored by using a quartz crystal microbalance. The thickness of deposited gold was 3 nm or 20 nm.

After the vapor-deposition of gold, the samples, which were prepared at a substrate temperature of 0 or 20 °C, were heated at 40 °C for 1 h or 50 °C for 10 min in air.

The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and visible spectroscopy (VIS). XRD patterns were measured by the 2θ method using Cu-Kα radiation on Rigaku RINT-2000 system equipped with a thin film attachment. The incident angle of X-rays to the samples was 1°. TEM images were observed using a JEOL JEM-2010 transmission electron microscope operated at 200 kV, which was equipped with a Voyager microanalysis system from Noran Instruments. The samples were dissolved in methanol (guaranteed reagent, Nacalai Tesque), and drops of the solutions were placed on carbon-coated Cu grids and were dried. The morphology of the vapor-deposited gold on the surface of the PEO-NH_2 or PEG film was also observed by TEM. Carbon films were vapor-deposited onto the samples to fix the vapor-deposited gold layer on the surface. Then, the carbon films were stripped by dissolving the polymers in water, and were placed on Cu grids. VIS spectra were measured by UVDEC-660 spectrophotometer (Japan Spectroscopic Co, Ltd.).

Variation of the VIS spectra with increasing heat-treatment temperature was measured by using an optical absorption measuring system which was set up in our laboratory. Details of the system were described in a previous paper.[15]

X-Ray photoelectron spectroscopy (XPS) was carried out to evaluate the depth profiles of gold in the samples. XPS spectra were measured using Mg-Kα radiation on a Shimadzu ESCA-750. Depth profiling was achieved by a sequence of measurement of XPS and argon ion sputtering. The intensity of the Au $4f_{7/2}$ signal was plotted as a function of sputtering time.

To estimate the molecular motions of the polymer ($PEO-NH_2$), T_2 (spin–spin relaxation time) measurements were carried out by using a pulse ^1H NMR spectrometer (JEOL HMN-MU-25). Free induction decays were recorded for the total ^1H of the polymer in the temperature range -70 to 60 °C, and analyzed using a personal computer. The solid echo method was used for measurements below 40 °C. The Carr–Purcell–Meiboon–Gill method was used for measurements at 40 °C or above.

Results and discussion

1 Dispersion of gold particles into a melt

Fig. 1 shows the VIS spectra of a gold/$PEO-NH_2$ film and a gold/PEG film. These films were produced at the same time by vapor-deposition of gold (with a thickness of 20 nm) onto a melt of each polymer at 60 °C. In the usual thermal relaxation technique, when the thickness of the vapor-deposited gold exceeds 20 nm, dispersion of the nano-sized gold particles is incomplete. Therefore, we used films with a thickness of 20 nm in this study.

The gold (20 nm)/$PEO-NH_2$ film had an absorption band at 524 nm and showed a ruby-red color which is characteristic for nano-sized gold particles.[16] The band at 524 nm was assigned to the plasmon resonance absorption band of the nano-sized gold particles, according to previous results.[14,15] The peak wavelength of 524 nm suggested that the gold particles were dispersed separately from each other in the $PEO-NH_2$ film. This was confirmed by a TEM image of the gold/$PEO-NH_2$ film (Fig. 2). A dispersion of nanometer-sized particles was observed in the $PEO-NH_2$ film. The existence of gold was confirmed by elemental microanalysis and electron diffraction. The size distribution of the gold particles obtained from the TEM images was *ca.* 3.9 nm ± 1.7 nm.

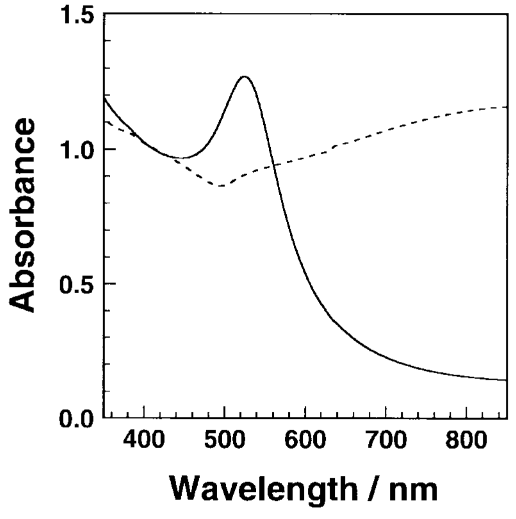

Fig. 1 VIS spectra of gold vapor-deposited on melts of $PEO-NH_2$ (solid line) and PEG (dashed line).

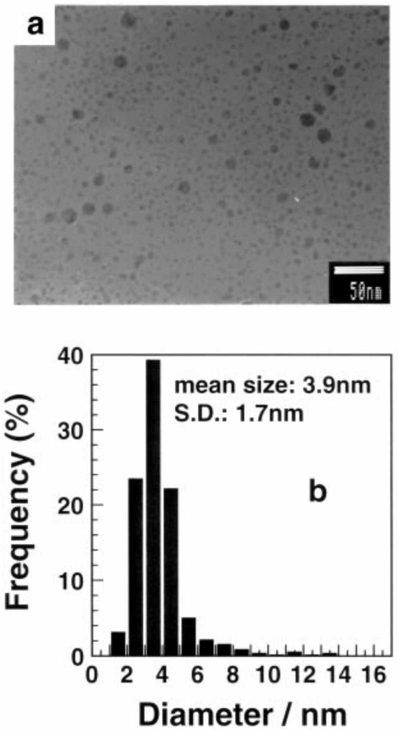

Fig. 2 (a) TEM image and (b) size distribution of gold particles dispersed in $PEO-NH_2$.

On the other hand, gold vapor-deposited onto a melt of PEG formed only conglomerates (Fig. 3), and thus the gold/PEG film exhibited a gold coloration and a broad VIS spectrum (Fig. 1). The difference between $PEO-NH_2$ and PEG was only in the terminal groups. Therefore, NH_2 groups are considered to contribute to the dispersion of the nano-sized gold particles into the $PEO-NH_2$ film.

The nano-sized gold particles dispersed in the $PEO-NH_2$ film were very stable for more than a year, and they are considered to be a kind of composite. The composite was readily soluble in water or other kinds of solvents, and gave a colloidal solution which was also stable for more than a year. The solid composite was recovered from the colloidal solution by evaporating the solvent, and the recovered composite readily dissolved in solvents again. These are the advantages of composite prepared by the present procedure.

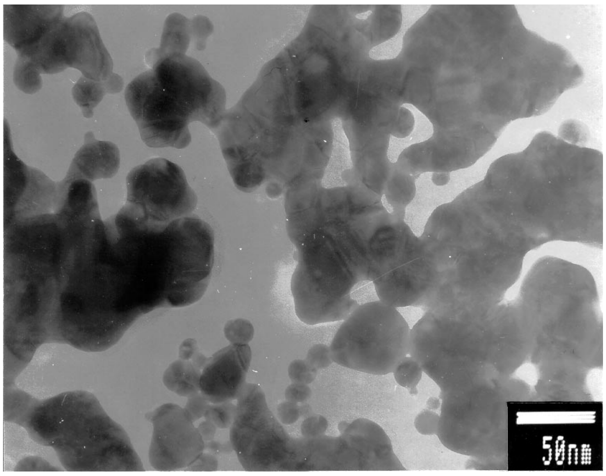

Fig. 3 TEM image of gold vapor-deposited on a melt of PEG.

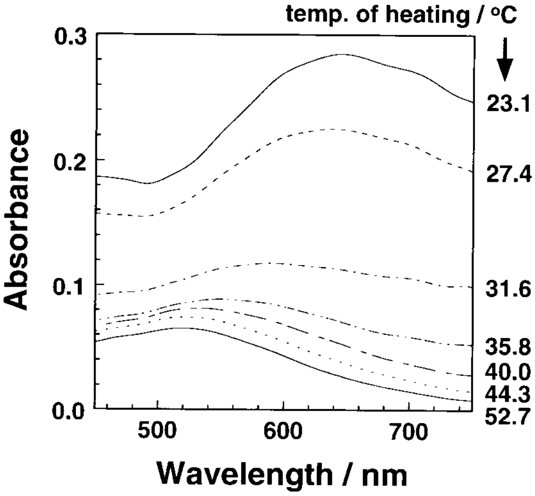

Fig. 4 Variation of the VIS spectrum of a gold (3 nm)/PEO-NH_2 film with increasing heat-treatment temperature.

2 Dispersion of gold particles from a gold layer formed on a solid polymer

For a further study on the dispersion of gold particles into polymer films, we examined the vapor-deposition of gold onto solid films of PEO-NH_2 and PEG. The dispersion behavior was investigated from the variations of VIS spectra and the morphology of gold deposited with increasing heat-treatment temperature.

2.1 Dispersion behavior of gold on a PEO-NH_2 film. Fig. 4 shows the variation of VIS spectra of a gold (3 nm)/PEO-NH_2 film with the heat-treatment temperature. The film was formed by the vapor-deposition of gold with a thickness of 3 nm onto a PEO-NH_2 film kept at 20 °C, and VIS spectra were measured sequentially on the same sample. The gold (3 nm)/PEO-NH_2 film initially showed a broad band at *ca.* 640 nm. With increasing heat-treatment temperature, the band shifted toward shorter wavelengths (blue-shift) and the absorbance decreased. As the heat-treatment temperature rose above the melting point of PEO-NH_2, the band showed a constant peak at 520 nm.

Fig. 5 shows TEM images of the gold (3 nm)/PEO-NH_2 films. The vapor-deposited gold formed nano-sized particles on the surface of the PEO-NH_2 film [Fig. 5(a)]. Thus the absorption band observed at 640 nm in the initial gold(3 nm)/PEO-NH_2 film was the plasmon band of the gold particles. The band was broadened and red-shifted compared to that of well-isolated gold particles, because the particles having complex shapes were compacted on the surface of the PEO-NH_2 film.[4]

As the heat-treatment temperature rose, the morphology of the gold particles changed. Upon heat-treatment at 40 °C for 1 h, the gold particles coalesced and increased in size, and the particles still remained on the surface of the PEO-NH_2 film [Fig. 5(b)]. At 40 °C, PEO-NH_2 was in a mixed state of solid and melt. The increase in the particle size brought about an increase in the distance between particles, and hence a decrease in the electronic interactions between the gold particles. Therefore, the VIS spectra showed a blue-shift. The changes of the morphology of the gold particles also brought about a decrease in scattering of light, and thus the absorbance was decreased.

Depth profiles of gold in the gold/PEO-NH_2 film, which was obtained from XPS data, are shown in Fig. 6. The high intensity of the Au $4f_{7/2}$ signal at the start of the sputtering for the initial gold/PEO-NH_2 film indicated that gold was located on the surface of the film. The profile of gold in the gold/PEO-NH_2 film heat-treated at 40 °C was similar to that in the initial film.

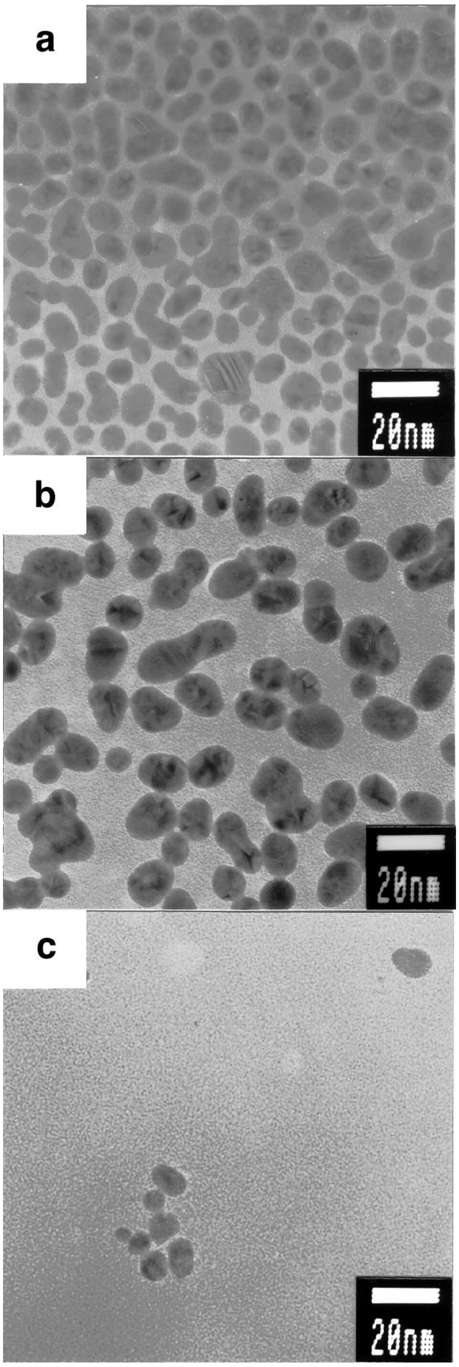

Fig. 5 TEM images of gold (3 nm)/PEO-NH_2 films, (a) as deposited, (b) after heat-treatment at 40 °C for 1 h, and (c) after heat-treatment at 50 °C for 10 min.

Upon heat-treatment at 50 °C (above the melting point of PEO-NH_2), the morphology of the gold/PEO-NH_2 film showed a remarkable change. Coagulated gold particles were observed on the surface of the film [Fig. 5(c)], but the number of coagulated particles was extremely small compared to that observed on the initial film. The depth profile showed a flat distribution of gold in the PEO-NH_2 film (Fig. 6). This indicated that the gold particles were dispersed within the PEO-NH_2 film. The dispersion of the gold particles led to a further increase in the distance between each particle, and thus the VIS spectra showed the plasmon band at 520 nm.

The results described above suggested that the dispersion of the gold particles into the PEO-NH_2 film did not occur until the PEO-NH_2 melted completely.

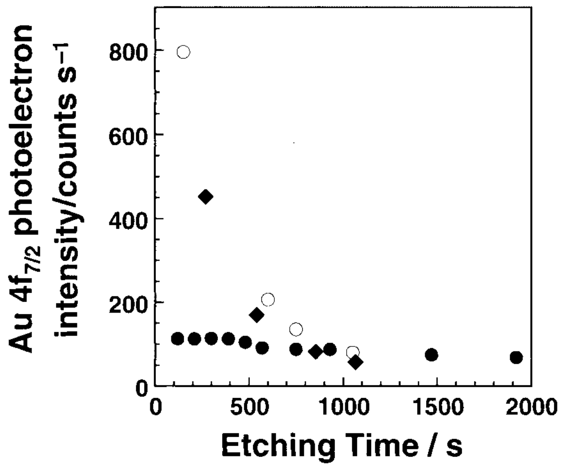

Fig. 6 Depth profile of gold in a PEO-NH_2 film.

2.2 Dispersion behavior of gold on a PEG film. In a gold (3 nm)/PEG film, gold produced conglomerates on the surface of the PEG film kept at 20 °C. After heat-treatment at 40 °C, the conglomerates coalesced and formed islands. Even after heat-treatment at 50 °C, these islands remained on the surface. The gold (3 nm)/PEG film did not show the plasmon band or any spectral change in a series of VIS spectra (Fig. 7), and dispersion of the gold particles into the PEG film was not observed at all. Vapor-deposition of gold at a substrate temperature of 0 °C brought about the formation of nano-sized particles on the surface of the PEG film. However, the dispersion of the gold particles did not occur.

2.3 Dispersion behavior of gold deposited with a thickness of 20 nm. When the thickness of vapor-deposited gold was increased to 20 nm, gold formed large conglomerates on the surface of the PEO-NH_2 film kept at 20 °C. In comparison with the gold vapor-deposited onto the melt, the thickness of gold (20 nm) deposited on to the solid PEO-NH_2 film was too great to produce nano-sized particles on the surface of the film. The plasmon band of the nano-sized gold particles did not appear in a series of VIS spectra measured with increasing heat-treatment temperature (Fig. 8). This indicated that the gold particles were not dispersed from the conglomerates of gold, even upon heat-treatment above the melting point.

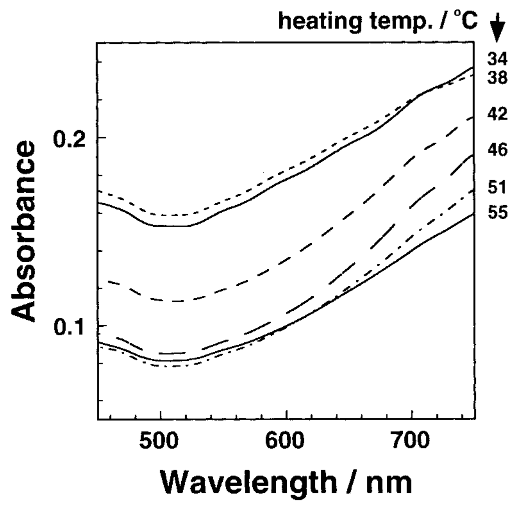

Fig. 7 Variation of the VIS spectrum of a gold (3 nm)/PEG film with increasing heat-treatment temperature.

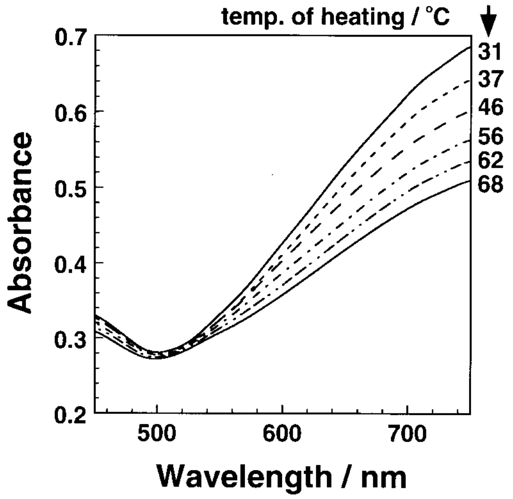

Fig. 8 Variation of the VIS spectrum of a gold (20 nm)/PEO-NH_2 film with increasing heat-treatment temperature.

3 Investigation of the molecular motion of PEO-NH_2

In the present study, the gold particles were not dispersed below the temperature where the PEO-NH_2 film melted completely. On the other hand, in previous reports, nano-sized gold particles were dispersed into a vapor-deposited nylon-11 film below the melting point (mp = *ca.* 100 °C).[15] We considered that this difference in the dispersion behavior arose from the difference in the molecular motion of the polymers.

Measurement of the spin–spin relaxation time (T_2) of ^1H is very useful for evaluating the molecular motions of polymers.[17,18] A solid polymer usually consists of various phases such as crystal, amorphous phase, and the interface of the crystal and amorphous phases. In these phases, the motions of molecules have different T_2 values.[19] T_2 values are of the order of 10^{-5} s for molecules contained in a crystal phase, in the range 10^{-3}–10^{-2} s in an amorphous phase, 10^{-4}–10^{-3} s in the interface between the crystal and the amorphous phase, and over 10^{-2} s in a melt, respectively.

The gold particles began to disperse into the vapor-deposited film of nylon-11 at 60–70 °C. In this temperature range, T_2 of the vapor-deposited nylon-11 was *ca.* 3×10^{-3}–4×10^{-2} s. This indicated that there was significant molecular motion of the vapor-deposited nylon-11 even in the solid state.

Fig. 9 shows the temperature dependence of T_2 for PEO-NH_2. Below −20 °C, PEO-NH_2 consisted of a crystal phase showing a single component with a T_2 of *ca.* 1×10^{-5} s. In the range from −20 °C to less than 40 °C, PEO-NH_2

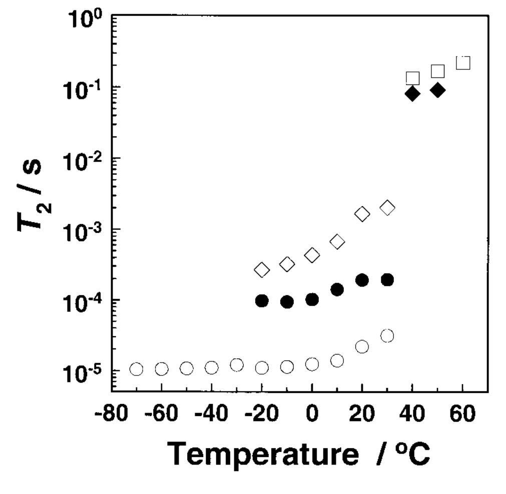

Fig. 9 Temperature dependence of T_2 of PEO-NH_2 measured by pulse ^1H NMR.

had three components corresponding to the crystal phase ($T_2 = ca.\ 1\times10^{-5}$–$3\times10^{-5}$ s), an amorphous phase ($T_2 = ca.\ 2\times10^{-4}$–$2\times10^{-3}$ s), and the interface between them ($T_2 = ca.\ 1\times10^{-4}$–$2\times10^{-4}$ s). Evaluation of these phases showed that below the melting point of PEO-NH_2, the crystal phase was the major constituent (>70% at 30 °C) in the solid PEO-NH_2. This indicated that the molecular motion of PEO-NH_2 was highly restricted in the solid sate compared to the vapor-deposited nylon-11. Therefore, the nano-sized particles were not dispersed into the solid PEO-NH_2 film.

In previous research, polymers having large molecular weights were effective for protecting nano-sized metal particles.[8] Longenberger and Mills reported that the use of PEG having an average molecular weight of 20000 g mol^{-1} brought about the formation of nano-sized gold particles, but PEG having an average molecular weight of 3350 or 1450 g mol^{-1} was not effective for preparing nano-sized particles. However, in our study, PEO-NH_2 with an average molecular weight of *ca.* 2000 was effective, but polymers such as poly(vinylpyrrolidone) or PEG having high molecular weights were not effective for preparing gold particles by the vapor-deposition process. In our procedure, the dispersion of the gold particles requires the molecular motion of the melted polymer, so that polymers having relatively small molecular weights are favorable.

Conclusions

Nano-sized gold particles were prepared by using a melt of PEO-NH_2 as a matrix. The difference in the dispersion behavior exhibited by PEO-NH_2 and PEG indicated that the NH_2 group was effective for dispersing the nano-sized gold particles into the PEO-NH_2 film.

The results, which were obtained by examining the vapor deposition of gold onto solid polymer films, indicated that the dispersion of the nano-sized particles was dependent on the morphology of the deposited gold, in addition to the effect of the polymer terminal substituent (NH_2). The gold was required to be deposited on the PEO-NH_2 film as the particles separated from each other in order to be dispersed into the film as nano-sized particles.

The dispersion of the vapor-deposited gold occurred only above the melting point of PEO-NH_2. Pulse ^{1}H NMR measurements indicated that the molecular motion of PEO-NH_2 was restricted in the solid state compared to vapor-deposited nylon-11. Therefore, the nano-sized particles were not dispersed into the solid PEO-NH_2 film. The present results suggest that significant molecular motion of a polymer is required for dispersing gold particles into a polymer film.

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Paper 9/00012G